

# EXCITATION OF HYDROGEN MOLECULES BY ELECTRON IMPACT

by

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## ABSTRACT

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Using one-center wave functions of Huzinaga for the hydrogen molecule together with the Born and Ochkur approximations, the excitation of the molecule from the ground state to the B and C electronic states by electron impact has been investigated. The shape of the curves for the differential cross section and for the oscillator strength is in accord with the experimental results of Geiger. The effect of exchange is to reduce the scattering cross sections.

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## I. INTRODUCTION

Since the molecular potential is not spherically symmetrical, the theoretical investigation of the scattering of electrons by molecules is more difficult in comparison with similar investigations for atomic targets. Using Born approximation, Massey and Mohr<sup>1</sup> have evaluated cross sections for the excitation of the hydrogen molecule by electron impact from the ground state  $X(1s\sigma^2 \Sigma_g^+)$  to the lowest stable excited state  $B(2p\sigma \Sigma_u^+)$ . They employed two-center wave functions of Wang<sup>2</sup> and of Guillemin and Zener<sup>3</sup> for the ground state and for the excited state respectively. Similar investigations were carried out by Roscoe<sup>4</sup> for the excitation of the molecule to  $B(2p\sigma \Sigma_u^+)$ ,  $C(2p\pi \Pi_u)$ ,  $D(3p\pi \Pi_u)$  and  $X(2s\sigma \Sigma_g^+)$  states. For the excited states MacDonald's<sup>5</sup> wave functions were used in which the inner electron is being referred to the two nuclei and the center of the molecule is the origin of the co-ordinates for the excited electron. Even with such simple wave functions approximations were used to evaluate the multi-center integrals. Recently Khare and Moiseiwitsch<sup>6,7</sup> have employed two-center wave functions for the investigation of the elastic scattering of electrons by molecular hydrogen and the dissociation of the hydrogen molecule due to electron impact but there again to avoid lengthy computation the integrals were evaluated for large internuclear separation. However all such integrals can be easily evaluated if one-center wave functions are used for both the initial and final states of the molecule. With such a treatment the effect of exchange may also be included by the use of some simple exchange approximation like that proposed by Ochkur<sup>8</sup>.

Recently Geiger<sup>9</sup> has carried out experimental investigation on the excitation of hydrogen molecule by high energy (25 kev) electron impact. Because of low energy resolution, the differential cross sections and the generalised oscillator strengths are given as the sum for the excitation of the hydrogen molecule to the B and C states. The shape of the experimental curves shows a fair agreement with the theoretical results of Roscoe<sup>4</sup> but at small angles of scattering the experimental values are 20 - 30 % higher. It is of interest to examine the problem using one-center wave functions which allows all the integrals to be evaluated exactly and with little labor.

## II. THEORY

According to the first Born approximation the differential cross section for the electronic excitation of the hydrogen molecule by an electron having  $\underline{k}_0$  and  $\underline{k}_n$  as the initial and final wave vectors is given by<sup>10</sup> (cf. Peek<sup>11</sup>)

$$I_n^D(\omega) = \frac{16}{k^4} \frac{k_n}{k_0} \left\{ \frac{1}{4\pi} \int_0^\pi \int_0^\pi \int_0^\pi |E(\underline{k}, R, \delta, \eta)|^2 |X_0(R)|^2 R^2 \times \sin \delta \, d\delta \, d\eta \, dR \right\} \quad (1)$$

where  $\underline{K}$  is the change in the wave vector of the incident electron which lies after scattering between the solid angle  $\omega$  and  $\omega + d\omega$ ,  $R$  is the internuclear distance,  $\delta$  and  $\eta$  are the polar angles which fix the internuclear axis  $\underline{R}$  with respect to  $\underline{K}$ ,  $X_0(R)$  is the initial vibration wave function and

$$E(K, R, \delta, \varphi) = \int e^{i\mathbf{k} \cdot \mathbf{r}} \Psi_0(\mathbf{r}_1, \mathbf{r}_2, R) \Psi_n^*(\mathbf{r}_1, \mathbf{r}_2, R) d\mathbf{r}_1 d\mathbf{r}_2. \quad (2)$$

where  $\Psi_0$  and  $\Psi_n$  are the electronic wave functions of the initial and final states of the molecule respectively and the position vectors  $\mathbf{r}_1$  and  $\mathbf{r}_2$  of the molecular electron being referred to the center of the molecule. In deriving (1) it has been assumed that  $k_n$  and  $K$  do not depend upon the final rotational and vibrational states which remain unresolved. Further we assume that the electronic wave functions vary slowly with the internuclear distance  $R$  and  $|\chi_0(R)|^2$  has a strong maximum at the equilibrium internuclear distance  $R_0$  of the ground state. Hence (1) reduces to

$$I_n^D(\omega) = \frac{k_n}{R_0} \frac{16}{k^4} \langle |E(K, R_0)|^2 \rangle_{\text{av}} \quad (3)$$

where

$$\langle |E(K, R_0)|^2 \rangle_{\text{av}} = \frac{1}{4\pi} \int_0^\pi \int_0^{2\pi} |E(K, R_0, \delta, \varphi)|^2 \sin \delta d\delta d\varphi. \quad (4)$$

To include exchange we employ Ochkur<sup>8</sup> approximation according to which if  $f_n$  is the direct scattering amplitude for an electron scattered by the hydrogen molecule, the exchange scattering amplitude  $g_n$  is given by

$$g_n = \frac{k^2}{2R_0^2} f_n. \quad (5)$$

Since the ground state of the hydrogen molecule consists of two electrons bound in a singlet spin state, the differential cross section including exchange is given by

$$I_n(\omega) d\omega = \frac{k_n}{k_0} \left(1 - \frac{k^2}{2k_0^2}\right)^2 \frac{16}{k^4} \left\langle |E(k, R_0)|^2 \right\rangle_{av} d\omega. \quad (6)$$

Changing the variable of integration from  $\omega$  to  $K$  we obtain total excitation cross section

$$Q_n = \frac{32\pi}{k_0^2} \int_{k_{min}}^{k_{max}} \left(1 - \frac{k^2}{2k_0^2}\right)^2 \left\langle |E(k, R_0)|^2 \right\rangle_{av} \frac{dk}{k^3} \quad (7)$$

where

$$\left. \begin{aligned} k_{max} &= k_0 + k_n \\ k_{min} &= k_0 - k_n \end{aligned} \right\}. \quad (8)$$

and

If the energy of the incident electron is high (25 kev in the experimental investigation of Geiger<sup>9</sup>),  $k_n$  will be very close to  $k_0$  and the effect of exchange will be negligible. Under such conditions the differential cross section reduces to

$$I_n(K) = \frac{16}{K^4} \left\langle |E(K, R_0)|^2 \right\rangle_{av} \quad (9)$$

which is independent of  $k_o$  and  $k_n$ . The generalised oscillator strength  $F_n(k)$  may be expressed in terms of differential cross section by the following relation (cf. Mott and Massey<sup>12</sup>)

$$F_n(k) = (k_o^2 - k_n^2) K^2 g_n(k). \quad (10)$$

$F_n(k)$  reduces to oscillator strength for  $K$  equal to zero.

In the present investigation we take Huzinaga's<sup>13</sup> one-center wave functions given by

$$\begin{aligned} \Psi_o(r_1, r_2, R) = \frac{C_1}{\sqrt{2}} \left[ \phi_{in}^o(r_1) \phi_{out}^o(r_2) + \phi_{out}^o(r_1) \phi_{in}^o(r_2) \right] \\ + C_2 \phi_{er}^o(r_1) \phi_{er}^o(r_2) \end{aligned} \quad (11)$$

and

$$\Psi_{B,C}(r_1, r_2, R) = \frac{1}{\sqrt{2}} \left[ \phi_{in}^{B,C}(r_1) \phi_{out}^{B,C}(r_2) + \phi_{out}^{B,C}(r_1) \phi_{in}^{B,C}(r_2) \right] \quad (12)$$

where

$$\begin{aligned} \phi_{in}^o(r) &= C_3 \left[ N(1, \eta_1) e^{-\eta_1 r} Y_{00} + \delta N(4, \eta_2) r^3 e^{-\eta_2 r} Y_{00} \right. \\ &\quad \left. + \lambda N(4, \eta_2) r^3 e^{-\eta_2 r} Y_{20} \right] \\ \phi_{er}^o(r) &= N(2, \xi) r e^{-\xi r} Y_{10} \\ \phi_{out}^o(r) &= N(1, \eta_1) e^{-\eta_1 r} Y_{00} \end{aligned} \quad (13)$$

$$\left. \begin{aligned}
 \phi_{in}^{B,C}(\tau) &= p_1 N(1, \alpha) e^{-\alpha \tau} Y_{00} + p_2 N(4, \beta) r^3 e^{-\beta \tau} Y_{00} \\
 &\quad + p_3 N(4, \beta) r^3 e^{-\beta \tau} Y_{20} \\
 \phi_{out}^B(\tau) &= N(2, \eta_2^B) \tau e^{-\eta_2^B \tau} Y_{10} \\
 \phi_{out}^C(\tau) &= N(2, \eta_2^C) \tau e^{-\eta_2^C \tau} \frac{1}{\sqrt{2}} (Y_{11} + Y_{1\bar{1}}) \\
 N(n, x) &= \frac{(2x)^{n+1/2}}{\sqrt{(2n)!}}
 \end{aligned} \right\} \quad (13)$$

and  $Y_{\ell m}$  are the normalised spherical harmonics. The electronic wave function of the C state takes into account the fact that the state is doubly degenerate. For R equal to 1.4, which is equilibrium inter-nuclear distance of the ground state, the values of the various parameters occurring in the above wave functions are as follows<sup>14</sup>:

$$\left. \begin{array}{lll}
 C_1 = 0.99560365 & \eta_1 = 0.8 & \eta_2^B = 0.520 \\
 C_2 = -0.09366858 & z = 1.6 & \eta_2^C = 0.436 \\
 C_3 = 0.489949475 & p_1 = 0.761157 & \\
 \delta = 0.524208 & p_2 = 0.253422 & \\
 \lambda = 0.273048 & p_3 = 0.110674 & \\
 q_1 = 1.1 & \alpha = 1.1 & \\
 q_2 = 4.3 & \beta = 4.3 &
 \end{array} \right\} \quad (14)$$

As the values of  $\eta_2^B$  and  $\eta_2^C$  are not given by Huzinaga<sup>13</sup> at R = 1.4, they have been determined variationally.

Employing (7) to (13) and carrying out the integration, we obtain expressions for the differential and the total cross sections and the generalised oscillator strength. As the final expressions are quite lengthy they need not be given here. However, it may be mentioned that

both for B and C states the differential cross section, which can be obtained analytically, falls as  $K^{-2}$  for small  $K$  and as  $K^{-14}$  for high  $K$  thus resembling the  $1p$  state of helium from which they derive. The high  $K$  behaviour of the present differential cross section for B state thus differs from that obtained by Roscoe<sup>4</sup> where the cross section falls as  $K^{-12}$ .

### III. RESULTS AND DISCUSSIONS

To have an idea of the usefulness of the present one-center wave functions we have shown in Table 1 the energy values, threshold excitation potentials, and diamagnetic susceptibility of the molecule at  $R = 1.4$  as obtained by employing (11) through (14). A comparison of the present values with those obtained by more elaborate one-center<sup>15</sup> and two-center<sup>16</sup> calculations and the experimental values<sup>9,17</sup> indicates satisfactory agreement and thus provides us some degree of confidence in the values of the scattering cross sections which are presented here.

In Figure 1, we have shown the sum of the differential cross sections for B and C states as obtained from (9) along with the experimental values of Geiger<sup>9</sup> and the theoretical values of Roscoe<sup>4</sup>. The shape of the curve is in fair agreement with the experimental values although the absolute experimental values lie in between the two theoretical curves. Such agreement should be regarded as satisfactory, particularly in view of the fact that the absolute experimental values has been obtained by normalizing the experimental data for the elastic scattering of the electrons by the hydrogen molecule with the theoretical values of Roscoe<sup>18</sup>. In Figure 1, for the sake of clarity, the differential



cross sections for the B and C states are not shown separately but they can be easily obtained from Figure 2 where the generalized oscillator strength is plotted as a function of  $\ln(k^2)$ . We have taken 12.6 ev to be excitation threshold potential for both B and C states as obtained by Geiger<sup>9</sup>. Taking excitation threshold potentials equal to those obtained from (11) and (12) does not change the results by any appreciable amount. From Figure 2, we notice that the oscillator strength for B and C states are 0.39 and 0.31 respectively. The value for the C state is in excellent agreement with the experimental value and lies in between the various theoretical values<sup>19</sup>, but the value for the B state is rather high as compared to the values obtained by other investigators, the reason for which remains obscure.

From Figure 3 we notice that the effect of exchange is to reduce the total cross section throughout the energy range of the incident electron but the reduction is appreciable only near the threshold of excitation. It may be further noted that the present cross sections are higher than those estimated by Craggs and Massey<sup>20</sup> from the differential cross sections given by Roscoe<sup>4</sup>.

Finally it may be mentioned that since satisfactory results have been obtained even with simple one-center wave functions as employed in the present investigation, such wave functions should find more place in the molecular scattering investigations<sup>21</sup>. Work is in progress with one-center wave functions for the excitation of the ground state hydrogen molecule to triplet excited states by electron impact.

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21. See also Ref. 15, Section III.

TABLE 1.  
ENERGY AND DIAMAGNETIC SUSCEPTIBILITY OF THE MOLECULAR HYDROGEN

	$E_O$	$E_B$	$E_C$	$E_B - E_O$	$E_C - E_O$	$\chi \times 10^6$ (in Gaussian Units)
<u>Theoretical</u>						
Huzinaga <sup>13</sup> (one-center)	-1.120566	-.678017 <sup>†</sup>	-.663181 <sup>†</sup>	.442549 <sup>†</sup>	.457385 <sup>†</sup>	-4.78 <sup>†</sup>
Bhatia & Temkin <sup>15</sup> (one-center)	-1.072879					-4.38 <sup>‡</sup>
Kolos & Roothaan <sup>16</sup> (two-center)	-1.174444	-.703744		.470700		-4.03
Experimental				.463 <sup>9</sup>	.463 <sup>9</sup>	-(3.9 - 4.0) <sup>17</sup>

$E_O$ ,  $E_B$  and  $E_C$  are the energies of the electronic states  $X(1\sigma^2 \Sigma_g^+)$ ,  $B(2\sigma\sigma \Sigma_u^+)$  and  $C(2\pi \pi \pi_u)$  respectively and their differences denote threshold of excitation potential at the internuclear distance equal to 1.4 •  $\chi$  gives diamagnetic susceptibility of the ground state of the hydrogen molecule.

<sup>†</sup>Values obtained in the present investigation.

<sup>‡</sup>Value kindly supplied by Dr. A. K. Bhatia.

FIGURE CAPTIONS

- Figure 1. Sum of the differential cross sections for the inelastic scattering of 25 kev electrons which excite the ground state hydrogen molecule to B and C electronic states: A - present; B - Roscoe<sup>4</sup>;  $\Theta$  - experimental points of Geiger<sup>9</sup>.
- Figure 2. Curves B and C give generalized oscillator strength for the excitation of the ground state hydrogen molecule by electron impact to the B and C electronic states respectively and S denotes their sum. For comparison, the experimental points  $\Theta$  of Geiger<sup>9</sup> for the sum and the curves, marked with the suffix R, obtained from the results of Roscoe are also shown.
- Figure 3. Total cross sections for the excitation of the ground state hydrogen molecule to the B and C electronic states by electron impact: D - Born Approximation; E - Born - Ochkur Approximation; F - Born cross section estimated by Craggs and Massey<sup>20</sup> from the differential cross sections of Roscoe<sup>4</sup>.

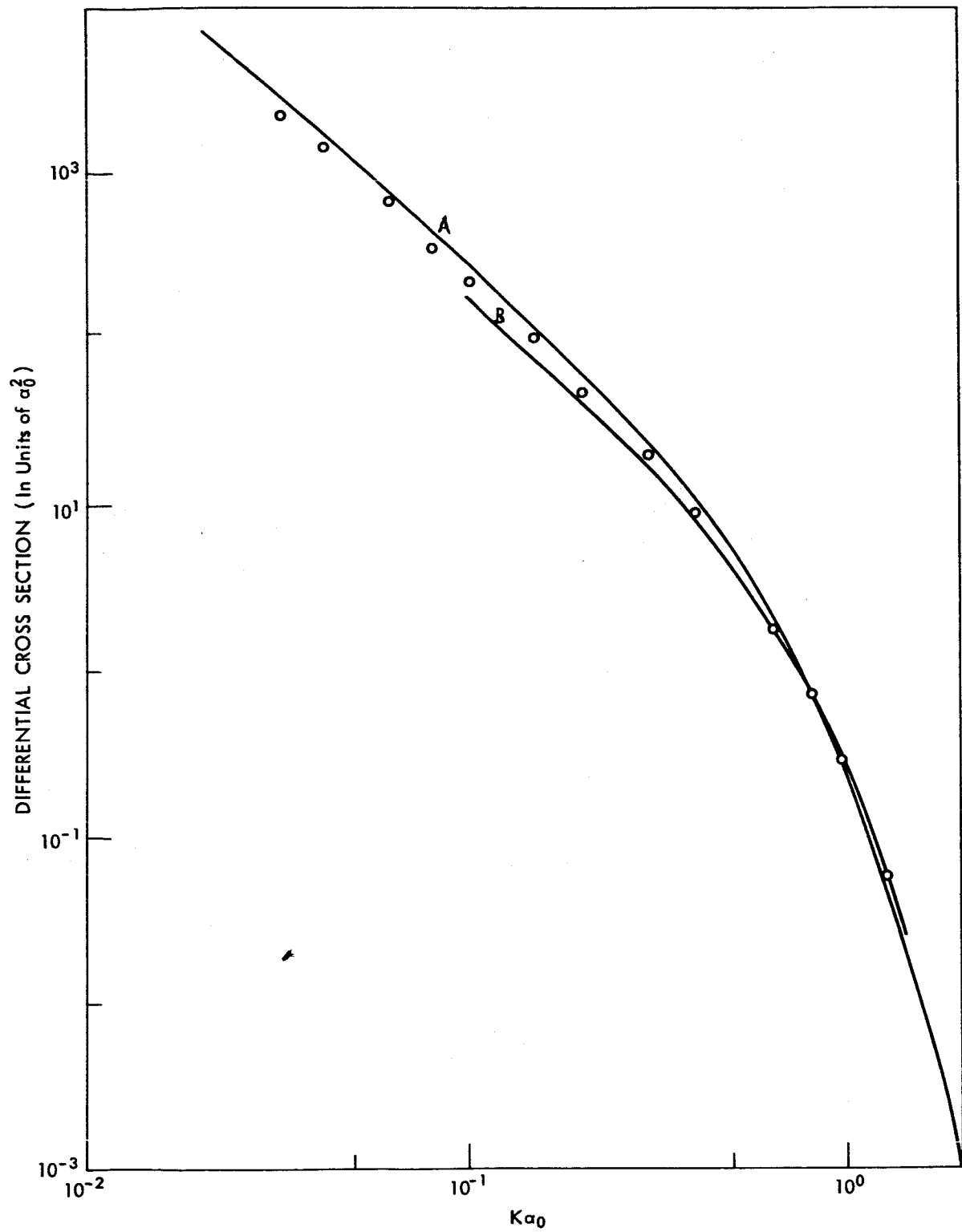


FIGURE 1.

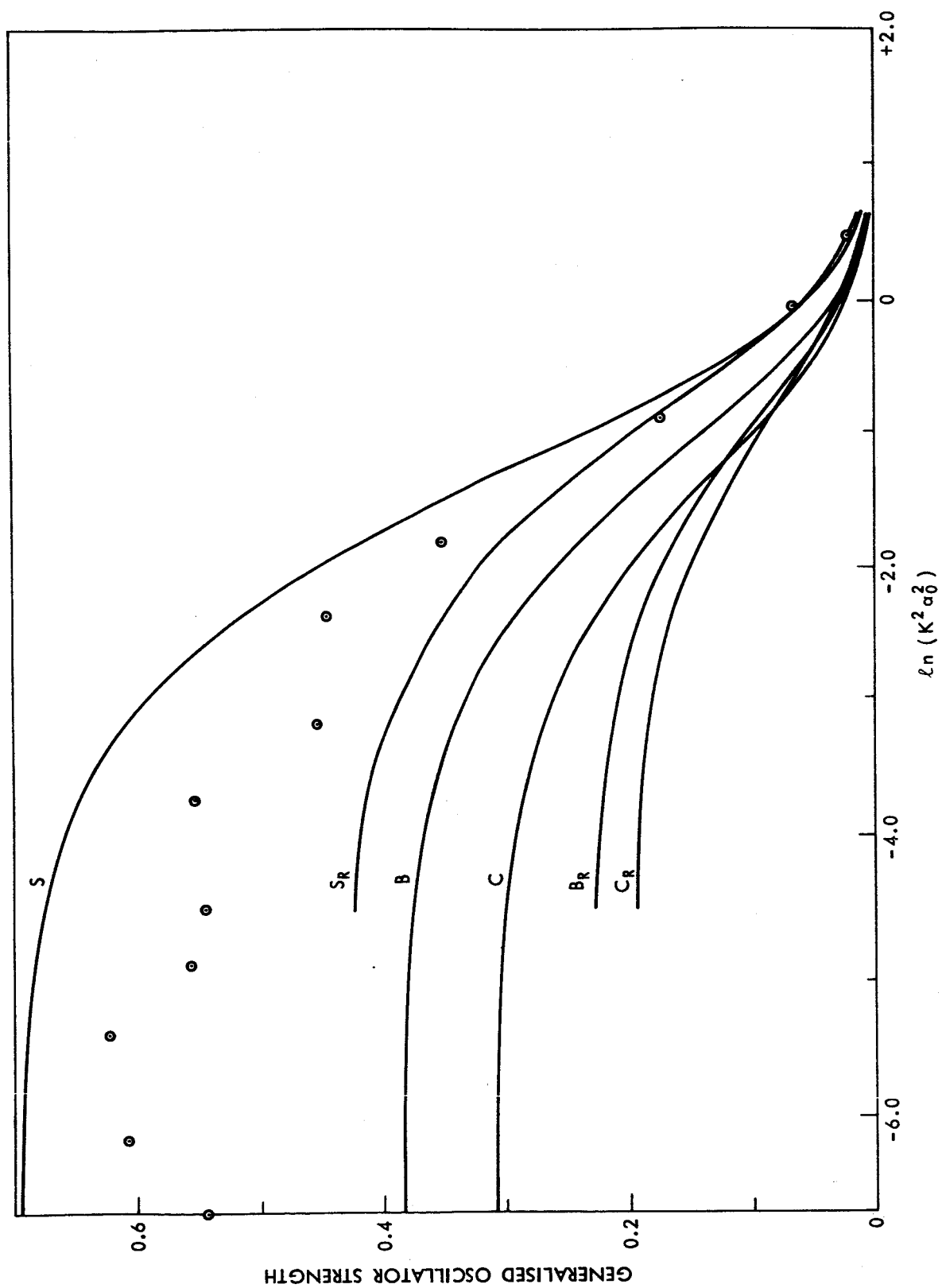


FIGURE 2.



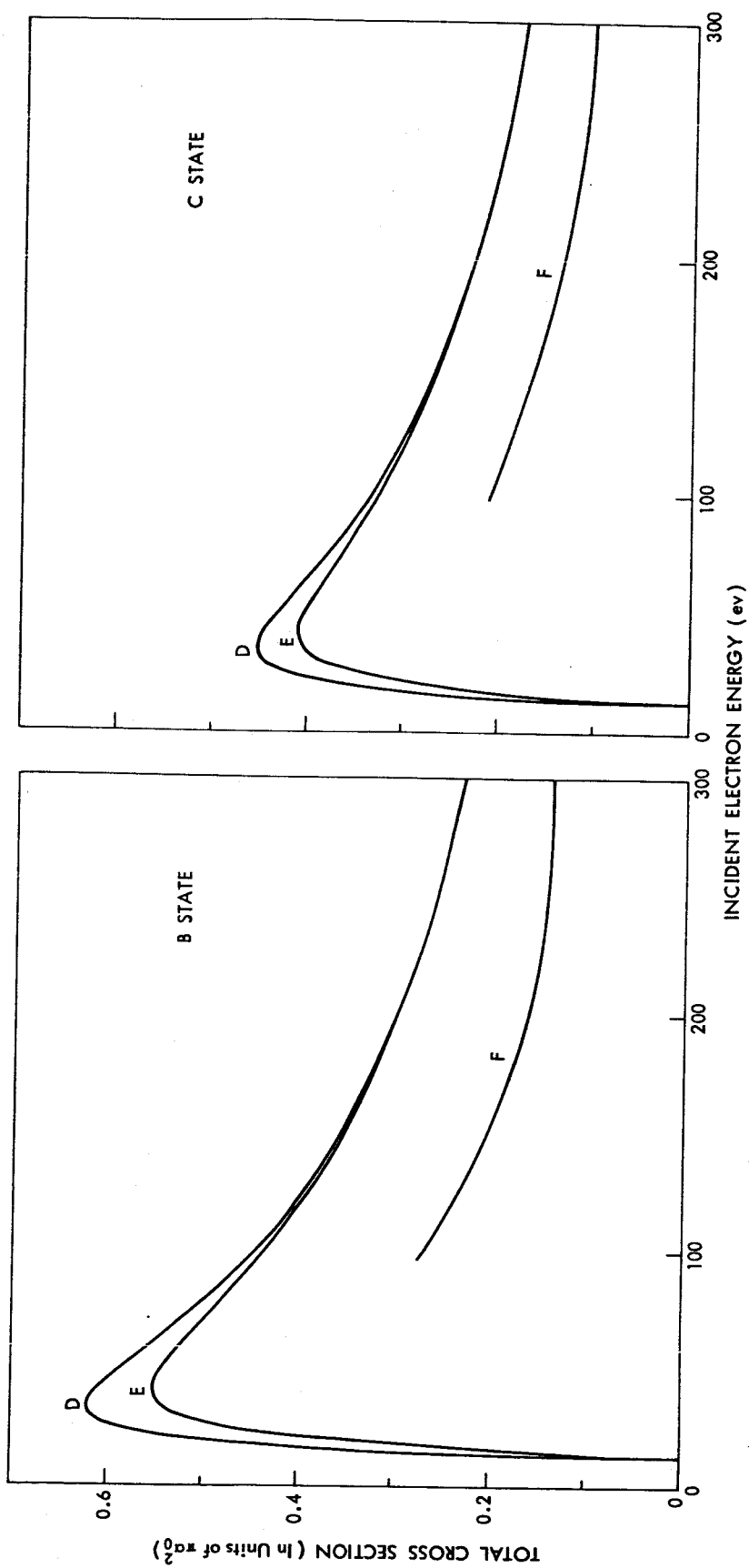


FIGURE 3.